Participation of Several Different Electronically-Excited Biradical Structures in the Ground States of Bicyclic Tricalicene and Tricyclic Tetracalicene (Commemoration Issue Dedicated to Professor Shigeo Tanimoto On the Occation of His Retirement)

AUTHOR(S):

Sugimoto, Toyonari; Sakaguchi, Masashi; Ando, Hiroshi; Arai, Yoshihisa; Tanaka, Tomohiro; Yoshida, Zen-ichi; Yamauchi, Jun

ISSUE DATE:

1992-10-30

URL:

http://hdl.handle.net/2433/77457

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 70, No. 3, 1992

COMMUNICATION

Participation of Several Different Electronically-Excited Biradical Structures in the Ground States of Bicyclic Tricalicene and Tricyclic Tetracalicene

Toyonari SUGIMOTO*, Masashi SAKAGUCHI*, Hiroshi ANDO*, Yoshihisa ARAI*, Tomohiro TANAKA*, Zen-ichi YOSHIDA*, and Jun YAMAUCHI**

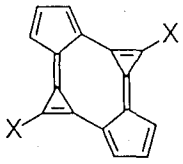
Received July 15, 1992

The solid ESR measurement of bis(*tert*-butylthio)-substituted derivatives of bicyclic tricalicene (**2**) and tricyclic tetracalicene (**3**), the next higher analogues of cyclic bicalicene (**1**), suggests that at least two and three different low energy electronically-excited biradical structures are involved for **2** and **3**, respectively.

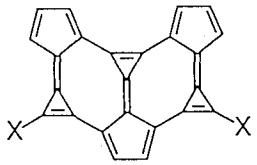
KEY WORDS: Cyclic polycalicene / ESR / Ground state / Electronically-excited biradical structure

The organic molecules, whose electronically-excited biradical structures are not so apart from the ground structure in energy, are of much interest in unique ground-state electronic structures as well as in novel optical, magnetical and electrical properties.[1] However, such examples are very rare. We have very recently reported participation of electronically-excited biradical structures in the ground states of cyclic bicalicene (**1a**) and its bis(*tert*-butylthio)-substituted derivative (**1b**),[2] which provide a first example evidenced in non-alternant hydrocarbon system.[3] The biradical structure in a low-energy singlet in thermal equilibrium with its counterpart triplet, makes a partial contribution to stabilization of ground-state electronic structure of **1** involving an energetically unfavorable antiaromatic 16π electron conjugation. This finding prompted us to investigate as to whether there is participation of electronically-excited biradical structures also in higher analogues of **1a**, bicyclic tricalicene (**2a**) and tricyclic tetracalicene (**3a**), in which cyclic bicalicene conjugation mode still preferentially contributes.[4] Herein we wish to report the evidence on such a participation from the ESR measurement of the bis(*tert*-butylthio)-substituted derivatives of **2a** and **3a**, (**3b** and **3b**).

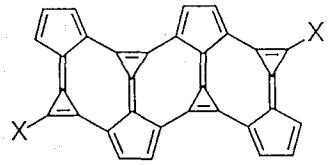
* 杉本豊成, 坂口雅史, 安藤 寛, 新井誉久, 田中知洋, 吉田善一:
Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606
** 山内 淳: College of Liberal Arts and Science, Kyoto University, Yoshida, Kyoto 606



1a: X=H
1b: X=SBu^t



2a: X=H
2b: X=SBu^t



3a: X=H
3b: X=SBu^t

The fresh microcrystalline solids of **2b** and **3b** obtained by recrystallization from $CHCl_3$–CH_3OH,[5] respectively, were used for the ESR measurement. In the solid ESR spectra at room temperature[6] one sharp and weak signal was observed near g= 2. However, by lowering temperature a remarkable change was observed in the spectra. Thus, for **2 b** at both wings of the central signal one pair of very weak signals appeared at 90 K, which are presumably due to fine structure of a triplet. The width between the signals is ca. 13 G.[7] On the other hand, when the ESR spectrum of **3 b** was measured at 169 K, the signal due to $\Delta m_s = \pm 2$ transition, which is also characteristic of a triplet, was observed near 1633 G albeit in very low intensity. These results strongly suggest involvement of electronically-excited biradical structures also in the ground states of **2 b** and **3 b**, as has already been realized in **1 a** and **1 b**.[3]

The temperature (T) dependence of the signal intensity (I)[8] was investigated (see Fig. 1a and 1b). The I value tends to gradually decrease with a lowering temperature till ca. 30–50 K, and then to reversely increase below the temperature. In comparison of such a I–T relation in **2b** and **3b** with that in **1b**, it should be noted that for the two former cyclic polycalicenes the I value still increases beyond room temperature, while for the latter case the maximum occurs at ca. 250 K and at the higher temperatures a gradual decrease in I is observed.[3] The I–T behavior in **2b** and **3b** can well be analyzed by assuming involvement of several low energy singlet biradicals in thermal equilibrium with their counterpart triplets together with an impurity monoradical. By using a Bleaney–Bowers equation relating between I and T,[9] i. e.,

$I = N_m g^2 \mu_B^2 \cdot 1/2(1+1/2)/3kT +$

$N_b(i) g^2 \mu_B^2 \cdot 1(1+1)/3kT\{1+1/3\exp(\Delta E_i/kT)]$, where N_m and $N_b(i)$ are amounts of a monoradical and an i-th biradical, respectively, μ_B is Bohr magneton, k is Boltzmann constant, and ΔE_i is energy separation between a low energy singlet and its thermally-accessible triplet of an i-th biradical, the values of N_m, $N_b(i)$ and ΔE_i were determined so as to fit the calculated I–T curve with the observed one. The simulation demonstrates that the two and three biradicals are at least involved in **2b** and **3b**, respectively.[10] This makes remarkable contrast to involvement of one biradical in **1b**.[3] The $N_b(i)$ and ΔE_i values of each biradical involved in **2b**, **3b** and also for comparison **1b** are summarized in Table 1.[11] For **2b** and **3b** such a biradical (b_1) with a large ΔE(2–3 kcal/mol) participates that is not involved in **1b** at all. On the other hand, the second biradical (b_2) with the smaller ΔE value of 600–800 cal/mol is involved in each cyclic polycalicene. The contribution of b_1 to the ground

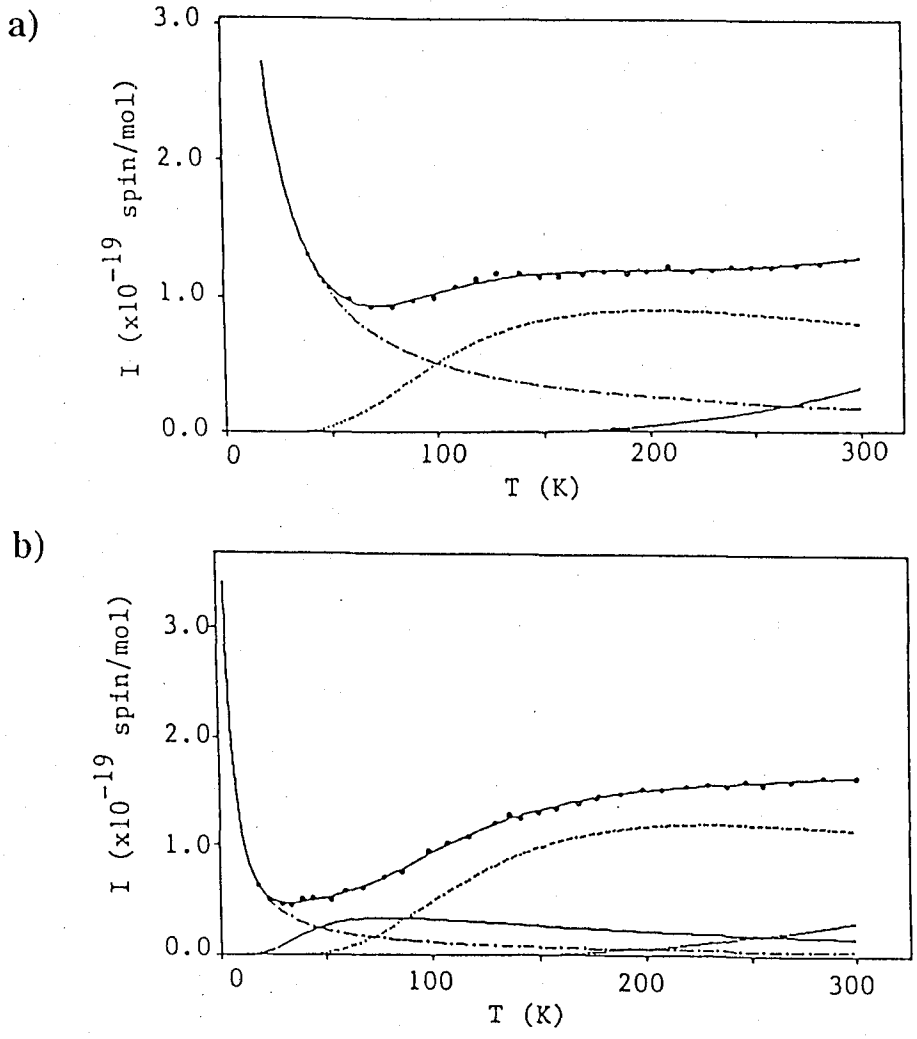


Fig. 1. The temperature (T) dependence of the central signal intensity (I) in the ESR spectra of (a) **2b** and (b) **3b**, and the separation to each contribution due to electronically-excited biradicals in low energy singlet states (——, ···· and ·· ··) and due to an impurity monoradical (—·—) : (•) the observed I at a given temperature and (—) the calculated T dependence of I.

Table 1. The amounts of biradicals involved in the ground states of **2b**, **3b** and a referred **1b**, and the energy separation between the low energy singlet and its thermally-accessible triplet of each biradical.

cyclic polycalicene	Nb(1)[a]	ΔE_1[b]	Nb(2)[a]	ΔE_2[b]	Nb(3)[a]	ΔE_3[b]
2b	6.0×10^{19}	2940	6.2×10^{19}	640		
3b	2.2×10^{19}	2380	9.6×10^{18}	750	9.2×10^{17}	260
1b			2.3×10^{18}	810		

[a]molecules/mol. [b]cal/mol.

states of **2b** and **3b** is comparable to or slightly larger than that of b_2, as shown from comparison between the $N_b(1)$ and $N_b(2)$ values. Furthermore, **3b** also involves a small amount of the third biradical (b_3), whose ΔE value is very small (260 cal/mol). Judging from the amount and ΔE of the electronically-excited biradical structures involved, it is supposed that both b_1 and b_2 are apart in comparatively low and almost the same energy from both ground structures, while b_3 in **3b** is in higher energy compared with those of b_1 and b_2.[12] For the three biradicals the low energy spin state ia all singlet and its counterpart triplet is in thermal equilibrium with the singlet.

Indeed like **1a** and **1b**, **2b** and **3b** have also participation of electronically-excited biradical structures, respectively, which are in such a low energy as to participate to the ground states albeit in very small content of 0.01–0.00015 %. Eventually, cyclic polycalicene constructs a quite unique non-altermant hydrocarbon system having participation of low energy electronically-excited biradical structures in its ground state.

This research was supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency from the Ministry of Education, Science and Culture, Japan. We wish to thank Prof. Y. Maruyama and Prof. T. Inabe and H. Ogata (Institute for Molecular Science) for low temperature ESR measurement.

References and Notes

1) H. Hartmann, H.-D. Brauer, and H. Stiger, *Z. Physik. Chem.* (*N. F.*) **56**, 103 (1967) ; L. K. Montgomery, J. C. Huffman, E. A. Jurczak, and M. P. Grende, *J. Am. Chem. Soc.* **108**, 6004 (1986) ; J. Fabian and R. Zahradnik, *Angew. Chem.* **101**, 693 (1989) ; *Angew. Chem. Int. Ed. Engl.* **28**, 677 (1989).
2) T. Sugimoto, M. Shibata, S. Yoneda, Z. Yoshida, Y. Kai, K. Miki, N. Kasai, and T. Kobayashi, *J. Am. Chem. Soc.* **108**, 7032 (1986).
3) T. Sugimoto, M. Sakaguchi, H. Ando, Y. Arai, T. Tanaka, Z. Yoshida, J. Yamauchi, A. A. Bothner-By, and M. Lisicki, *J. Am. Chem. Soc.* **113**, 3193 (1991).
4) T. Sugimoto, M. Shibata, A. Sakai, H. Ando, Y. Arai, M. Sakaguchi, Z. Yoshida, Y. Kai, N. Kanehisa, and N. Kasai, *Angew. Chem.* **103**, 454 (1991) ; *Angew. Chem. Int. Ed. Engl.* **30**, 446 (1991).
5) Whereas **2b** was obtained as single crystals being suitable for the X-ray structure analysis, **3b** was polycrystalline.
6) The ESR spectra were also taken in frozen CH_2Cl_2 solution. The similar spectral pattern was observed.
7) This value corresponds to 2 D, where D is the zero-field splitting parameter.
8) The I value corresponds to the spin amount, which was determined by using TANOL as a reference.
9) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London* **A 214**, 451 (1952) ; D. Bijl, H. Kainer, and A. C. Rose-Innes, *J. Chem. Phys.* **30**, 765 (1959).
10) The I-T relation could not be investigated at higher temperatures than ca. 320 K, because **2b** and **3b** began to decompose gradually. The possibility of involvement of the other biradicals with a larger ΔE value can not be ruled out.
11) The N_m values are 1.8×10^{18}, 3.9×10^{17}, and 2.0×10^{17} molecules/mol for **2b**, **3b** and **1b**, respectively.
12) The lower is the energy of an electronically-excited biradical structure, i. e., the larger the participation in the ground state, the stronger becomes the interaction between the two spins of the biradical structure.